



Technologies for energetic exploitation of biodiesel chain derived glycerol: Oxy-fuels production by catalytic conversion

Carlo Beatrice^{a,*}, Gabriele Di Blasio^a, Maurizio Lazzaro^a, Catia Cannilla^b, Giuseppe Bonura^b, Francesco Frusteri^b, Francesco Asdrubali^c, Giorgio Baldinelli^c, Andrea Presciutti^c, Francesco Fantozzi^d, Gianni Bidini^d, Pietro Bartocci^d

^a CNR-IM, Istituto Motori, Via G. Marconi 4, 80125 Napoli, Italy

^b CNR-ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126 Messina, Italy

^c CIRIAF – Centro Interuniversitario di Ricerca sull'Inquinamento da Agenti Fisici, Università degli Studi di Perugia, Via Duranti, 67, 06125 Perugia, Italy

^d CIMIS – Consorzio Interuniversitario Macchine Impianti e Sistemi per l'energia, l'industria e l'ambiente, c/o Dipartimento di Ingegneria Industriale, Via Duranti 97, 06125 Perugia, Italy

HIGHLIGHTS

- ▶ A glycerol conversion in an oxy-fuel for diesel engine has been proposed.
- ▶ Hyflon[®] based catalysts supported on spherical silica have been developed.
- ▶ The impact of the oxy-fuel on the engine emissions and performance has been described.
- ▶ LCA of the oxy-fuel/diesel blend shows a lower impact than the one of neat diesel.

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ABSTRACT

The paper describes the results of a co-operative research project aimed at the energetic exploitation of the biodiesel derived glycerol. The research objective is the definition and validation of a synthesis process for conversion of glycerol in an oxygenated fuel additive (glycerol alkyl-ether) suitable for blending with diesel and biodiesel.

The employed facilities, methodologies and first results from engine tests are described, including a preliminary Life Cycle Assessment (LCA).

Etherification of glycerol with *tert*-butyl alcohol and isobutylene allowed to identify the suitable experimental conditions required to obtain a mixture predominantly composed of higher glycerol ethers (GEM). Novel catalysts, based on perfluorosulphonic ionomers as active species and spherical silica as support, were found to be stable and easy reusable allowing to obtain mixtures containing very low amount of monoethers and oligomers considered as undesired products.

Engine tests with blends of GEM in diesel fuels revealed good combustion and emission performances when compared both to neat diesel fuel and a blend diesel/biodiesel.

LCA analysis indicates that the GEM/diesel blend generates an environmental impact which is lower than the one of neat diesel.

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1. Introduction

Pending the large-scale production of second generation biofuels [1], in the near future the biodiesel production should increase in order to approach the EU target of biofuel consumption for the year 2020 [2]. As a result, also the production of glycerol, which is the main by-product of the transesterification process, will grow

proportionally. So, the question arises from a cost-effective and efficient use of such a glycerol surplus. The combustion of glycerol "as it is" would represent a desirable solution. Unfortunately, because of its detrimental physical and chemical properties, raw glycerol is hardly usable in conventional energy production plants, such as fuel burners or internal combustion engines (ICEs). However, a proper design of the burner and refractory combustion chamber could allow to effectively burn crude glycerol, although a high particulate matter concentration is detected at the exhaust [3]. Alternative routes for glycerol recovery are represented by its

* Corresponding author. Tel.: +39 0817177186; fax: +39 0812396097.

E-mail address: c.beatrice@im.cnr.it (C. Beatrice).

energetic upgrading into high value products, such as synthesis of gases [4] and oxygenate additives for gasoline, biodiesel and diesel fuels [5].

In order to increase the energetic exploitation of the biodiesel production chain, a co-operative research project was started in 2010, aimed at recycling the biodiesel-derived glycerol in energy generating systems. The project was partially founded by MiPAAF, the Italian Ministry of Agriculture, Food and Forestry. It consists of three research lines: (i) conversion of the raw glycerol in a fuel suitable for ICEs; (ii) pyrolysis of biomass soaked with glycerol for syngas production; (iii) combustion of glycerol in a flameless oxy-burner.

The first research line, described in the present work, is focused on the development of a synthesis process for converting glycerol in a fuel suitable for ICEs. The final goal should be the definition and validation of an etherification process of raw glycerol for the production of an oxy-fuel that can be blended with diesel and biodiesel. An industrially relevant route for the conversion of glycerol into oxygenated chemicals involves the etherification to *tert*-butyl ethers [6–8]. In particular, since mono-*tert*-butyl ethers of glycerol (MBG) have a low solubility in diesel fuel, the etherification of glycerol, taking place with a consecutive reaction path, should be mainly addressed towards the formation of a mixture of di- (DBG) and/or tri-ethers (TBG) [6–9].

The project aims at a complete evaluation of the production process (in laboratory scale), as well as the validation of the Glycerol–Ethers Mixture (GEM) of DBG and/or TBG as fuel in experimental engine tests, with two main advantages: (i) the increase of the energy and CO₂ Well-To-Wheel (WTW) factor of the biodiesel supply chain; (ii) the addition of a high-quality oxy-fuel in the mineral fuels which contributes to the reduction of pollutant emissions from diesel engines.

The GEM production process for glycerol exploitation was also subjected to Life Cycle Analysis (LCA), from which the impact to human health, quality of ecosystems, and resources has been evaluated. The present paper illustrates the employed facilities, methodologies and the results of the research activity.

2. Materials and methods

2.1. Catalytic systems for the conversion of glycerol into diesel fuel components

Several Hyflon[®]-SiO₂ catalysts (c.a. 20 wt.%) were prepared by the conventional incipient wetness method using an alcoholic solution of Hyflon[®] Ion S4X perfluorosulphonic ionomer (H730, Solvay Solexis) as acid precursor. As carriers, two spherical silica, MS3030 and ES70Y, characterized by surface area of 300 and 295 m² g⁻¹ respectively, were supplied by PQ Corporation (Liverpool, UK). In addition, a fumed silica, LM50 with surface area of 150 m² g⁻¹ was supplied by Cab-O-Sil Division-Rheinfelden. After impregnation, the catalysts were dried in air at 120 °C for 12 h. As a reference, Amberlyst[®] 15 “dry” resin (A-15) from Rohm and Haas was used. The investigated catalysts were characterized by different techniques in order to determine textural and morphological structure, thermal stability, loading of active phase and acid capacity.

2.1.1. Plant and catalytic process

Isobutylene 3.0 (IB) by GHC Gerling (Hamburg, Germany), *tert*-butyl alcohol (TBA) and commercial anhydrous glycerol (purity ≥99.5%) were used as reactants, deferring the problem of using raw glycerol after a first validation of the catalytic process. The etherification reaction was carried out in liquid phase in a lab-scale stainless steel “jacketed-batch” reactor of 300 cm³ (see Fig. 1) under a stirring frequency of 1200 min⁻¹ in order to limit the



Fig. 1. Experimental set-up for catalytic etherification of glycerol.

influence of external mass transfer phenomena. Experiments were performed by operating at different *tert*-butyl alcohol/glycerol ($R_{TBA/GLY}$) or isobutylene/glycerol ($R_{IB/GLY}$) molar ratio (2.5–5.0) and by employing a catalyst amount of 0.3–7.5 wt.% referred to the glycerol weight ($R_{cat/GLY}$) at variable reaction time (6–17 h). A well-defined amount of glycerol and dry catalyst were loaded into the reactor and, before the addition of TBA or IB, the reaction environment was flushed with nitrogen to remove the air. A known amount of *tert*-butyl alcohol or liquid isobutylene, previously fed into a graduated tank, was injected into the reactor under 5 bar of nitrogen pressure. At the end of the run, the reactor was cooled down by an ice-bath, thus allowing all the gas phase compounds to be condensed.

2.1.2. The experimental engine for the GEM validation

The preliminary validation of the fuel was carried out with a single cylinder diesel research engine, specifically designed for combustion studies. All engine components represent the state of the art of the engine technology. The engine, developed at the Istituto Motori, has a modern combustion system design, 0.47 l of displacement and four valves, derived from a reference Euro 5 compliant four cylinder engine for passenger cars. The engine is equipped with a common-rail injection system and a fully programmable electronic control unit (ECU) to allow the modification of the engine operating parameters. The test bench is fully instrumented for measuring indicated signals and analyzing exhaust gases.

Auxiliary systems for boost, cooling, lubrication, etc., are not coupled to the engine in order to allow for a maximum control of these parameters without influencing the load conditions. This approach offers flexibility pertaining to operating conditions, without forfeiting state-of-the-art technology. The engine layout is sketched in Fig. 2, while the main design characteristics are listed in Table 1. Additional details are described elsewhere [10].

In each test points, the thermodynamic conditions at engine system boundaries (temperature, pressure and gas flow rate) were stabilized running the engine for 10 min, then fuel consumption, emissions, operating parameters (temperature, pressure, etc.) and 160 consecutive indicated cycles were recorded.

2.2. Life Cycle Analysis

The environmental impact of the Glycerol Ethers Mixture (GEM) production, as mixture of DBG and TBG compounds, was evaluated

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